



Bioleaching mechanism of Co and Li from spent lithium-ion battery by the mixed culture of acidophilic sulfur-oxidizing and iron-oxidizing bacteria

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ABSTRACT

The bioleaching mechanism of Co and Li from spent lithium-ion batteries by mixed culture of sulfur-oxidizing and iron-oxidizing bacteria was investigated. It was found that the highest release of Li occurred at the lowest pH of 1.54 with elemental sulfur as an energy source, the lowest occurred at the highest pH of 1.69 with FeS₂. In contrast, the highest release of Co occurred at higher pH and varied ORP with S + FeS₂, the lowest occurred at almost unchanged ORP with S. It is suggested that acid dissolution is the main mechanism for Li bioleaching independent of energy matters types, however, apart from acid dissolution, Fe²⁺ catalyzed reduction takes part in the bioleaching process as well. Co²⁺ was released by acid dissolution after insoluble Co³⁺ was reduced into soluble Co²⁺ by Fe²⁺ in both FeS₂ and FeS₂ + S systems. The proposed bioleaching mechanism mentioned above was confirmed by the further results obtained from the experiments of bioprocess-stimulated chemical leaching and from the changes in structure and component of bioleaching residues characterized by XPS, SEM and EDX.

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1. Introduction

The secondary batteries, including nickel–cadmium, nickel metal hydride and lithium-ion batteries, are used extensively in various areas as rechargeable energy supplier. In consequence, the spent batteries have been generated and discarded in astonishing quantities (Qing and Jian, 2004; Pietrelli et al., 2005; Shin et al., 2005). These batteries are generally classified as hazardous waste because they contain heavy metals and other toxic matters (Shapek, 1995). The improving awareness of environmental problems associated with the spent batteries and the increasing concerns of interests associated with the recovery of the valuable metal elements contained make it desirable to find an economic and environmentally friendly process to treat and recycle these spent batteries (Nan et al., 2005; Freitas and Rosalem, 2005; Freitas et al., 2007; Yang, 2003).

The traditional techniques for treating the spent batteries mainly involve pyrometallurgical process, hydrometallurgical process or the combination of both (Bernardes et al., 2004). The great energy consumption, high cost, low efficiency and serious second pollution of pyro- and hydrometallurgical processes urge a turn to biotechnology strategy. In the mining industry, the bio-hydrometallurgical (bioleaching) processes have been gradually replacing the hydrometallurgical processes due to their higher efficiency, low cost and few requirements (Barrett et al., 1993;

McNulty and Thompson, 1990). Recently, bioleaching of the spent secondary batteries has attained great attention (Cerruti et al., 1998; Zhu et al., 2003; Zhao et al., 2008a, 2008b; Mishra et al., 2008).

The dissolution biochemistry of metal sulfides in mineral ores, sewage sludge, soil, sediment and fly ash follows only two pathways, which are determined by the acid-solubility of the sulfides: the thiosulfate pathway and the polysulfide pathway (Cui and Zhang, 2008). The bacterial cell can affect this sulfide dissolution by “contact” and “non-contact” mechanisms. The non-contact mechanism is basically exerted by planktonic bacteria, which oxidize Iron (II) in solution. The resulting Iron (III) somehow comes into contact with a mineral surface, where they are reduced, and re-enter the cycle. The contact mechanism takes into account that most cells attach to the surface of sulfide minerals. This means that the electrochemical processes resulting in the dissolution of sulfide minerals take place at the interface between the bacterial cell (wall) and the mineral sulfide surface. In both contact and non-contact mechanisms, the bacteria contribute to mineral dissolution by generation of the oxidizing agent, the Iron (III) ion, and by subsequent oxidation of the sulfur compounds resulting from the dissolution (Rohwerder et al., 2003).

Different from metal sulfides, the spent secondary batteries are characterized by metals oxides and metals hydroxides. As a result, the bioleaching mechanisms of the spent batteries may differ from that with sulfides which has been expounded well. However, there is no report available on the bioleaching mechanism of the spent batteries. Due to the most wide application and very expensive

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content of Co and Li, treatment and recovery of the spent lithium-ion batteries have become a very attractive subject (Xu et al., 2008; Paulino et al., 2008; Freitas and Garcia, 2007; Dorella and Mansur, 2007). The present study aims to interpret the bioleaching mechanism of Co and Li from the spent lithium-ion batteries by the mixed culture of sulfur-oxidizing and iron-oxidizing bacteria grown under different energy materials.

2. Methods

2.1. Spent lithium-ion secondary batteries and the content of Co and Li

The spent lithium-ion secondary batteries were kindly supplied by the individual students from Beijing Institute of Technology. They were manually cut up into different portions (Cerruti et al., 1998), the separated active cathodic and anodic materials containing Co and Li were mixed, ground by milling and sieved to obtain a mesh size of less than 200 μm (Mishra et al., 2008). The resulting powder was used for bioleaching experiments.

The resulting powder was digested by $\text{HF-HNO}_3\text{-HCl}$ digestion method (USEPA, 1995). The content of Co and Li in the powder was 131 mg/g and 60 mg/g, respectively, as determined by atomic absorption spectrophotometer.

2.2. Microorganism and medium

Both the sulfur-oxidizing and iron-oxidizing bacteria were screened from an old mining site (Anshan Mountain, Liaoning Province, North China). The basic medium was composed of $(\text{NH}_4)_2\text{SO}_4$, 2.0 g; KH_2PO_4 , 1.0 g; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 1.0 g; CaCl_2 , 0.25 g; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.18 g and distilled water, 1000 mL. For growing sulfur-oxidizing bacteria, elemental sulfur, 10.0 g, was added into the basic medium and the pH value was adjusted to 5.5 as a seed medium. For growing iron-oxidizing bacteria, FeSO_4 solution (30% in w/w, pH 2.0), 10 mL, was added into the basic medium and the pH was adjusted to 2.0 as a seed medium. For preparing bioleaching media of mixed bacteria, 4.0 g of different energy material [elemental sulfur (S) or pyrite (FeS_2) or $\text{S} + \text{FeS}_2$] was added into the basic medium and the pH was 5.5.

Each of acidithiobacillus was inoculated into respective seed medium and was cultured at 30 °C in a 2000 mL beaker, with abundant compressed air continually fed to supply CO_2 and O_2 . When color of seed medium with iron-oxidizing bacteria turned into red brown after 2–3 d incubation due to the formation of Fe^{3+} or pH value of seed medium with sulfur-oxidizing bacteria decreased below 2.0 due to the generation of H_2SO_4 , both the medium were utilized as inoculum in the bioleaching experiments.

2.3. Bioleaching of the spent batteries

2.3.1. Bioleaching experiments

Both acidithiobacillus were inoculated, respectively, in 100 mL of bioleaching media with different energy materials (5%, v/v) in the 250 mL Erlenmeyer flasks and were incubated in a shaker at 30 °C at 120 rpm. Inoculation of the low-pH seed media caused a decline of the pH value of bioleaching media from 5.5 to below 4.0. After 10–12 d culture, the pH decreased from 4.0 to about 1.0 in flasks containing 4.0 g/L sulfur (Flasks A), dropped to approximately 1.5 in the flasks with 2.0 g/L sulfur + 2.0 g/L FeS_2 (Flasks B), declined to around 2.0 in the flasks with 4.0 g/L FeS_2 (Flasks C). At that moment the pH of Flasks B and C was adjusted precisely to the same value (1.0) as Flasks A with 0.5 mol/L H_2SO_4 solution, and then 1 g of powder electrode materials was added, respectively, into Flasks A, B and C. The electrode-contained flasks were further incubated in the shaker to carry out the bioleaching.

During bioleaching, the Oxidation–Reduction Potential (ORP) value of the solutions was monitored for reflecting the generation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and their transformation, the pH value was measured for reflecting the balance between the bio-genetic sulfuric acid and its consumption, the concentration of Co and Li was determined for reflecting the bioleaching efficiencies. Sterile controls were performed in the absence of bacteria using filter-sterilized medium at initial pH of 5.5 or after the H_2SO_4 adjust to pH 1.0 synchronized with the above-mentioned Flasks A, B, C. All the experiments, including the sterile controls, were carried out in triplicates.

2.3.2. Contact or non-contact mechanisms identification

One gram of powder electrode materials was encapsulated in a little dialysis bag which is capable of blocking transport of macromolecular with molecular weight of 8000–15,000, and then dived into the Flasks A, B and C at pH 1.0. The concentration of Co and Li in solution was periodically measured and compared with the leaching ones not trapped. Dialysis bag allowed the small molecules such as H^+ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ through, cutting the bacteria out. By this way, the bioleaching bacteria were prevented from a direct contact with the electrode material, removing the contact mechanism of bioleaching. All the experiments were carried out in triplicates.

2.3.3. XPS, SEM and EDX analysis of electrode leaching residues

After bioleaching experiments, the electrode material residue in the dialysis bag was collected to avoid being contaminated by sulfur and FeS_2 , washed five times using deionized water, and then dried in a vacuum drier at 80 °C. The electrode leaching residues harvested from Flasks A, B, and C were analyzed by XPS and compared with the original sample, thereby the existence or non-existence of $\text{Co}^{2+}/\text{Co}^{3+}$ after leaching under different energy materials was studied. The change in morphology of electrode residues from different energy materials was characterized by SEM. The micro-area chemical composition variation in electrode residue from FeS_2 bioleaching system was analyzed by EDX.

2.4. Chemical simulation of bioleaching process

2.4.1. Chemical simulation of the dissolution of Co and Li by bio-acid

Sulfur bioleaching system (Flasks A) was used for bio-genetic sulfuric acid leaching experiment. After the pH value of medium decreased to 1.0 from about 4.0 due to bio-oxidation of elemental sulfur, 1 g of electrode materials was added for bioleaching by bio-genetic acid. At the same time, H_2SO_4 solution at pH 1.0 also received 1 g of electrode materials serving as chemical acid leaching. The pH value increased rapidly in the chemical acid leaching system due to the consumption of acid; however, the pH value of the bio-acid leaching system increased slowly even when kept constant owing to continuous production of H_2SO_4 via sulfur bio-oxidation. In order to simulate the bio-acid leaching process, a special chemical leaching process was established. In this case, H_2SO_4 solution was constantly added into the chemical leaching system to maintain synchronous pH changes with bio-acid leaching system. The content of Co and Li in the 3 leaching systems was determined. All the experiments were carried out in triplicates.

2.4.2. Chemical simulation of the dissolution of Co and Li by reduction of the bio-induced Fe^{2+}

In order to assess the role of Fe^{2+} catalyzed reduction in Co release in $\text{S} + \text{FeS}_2$ or FeS_2 bioleaching systems, the dissolution behavior of the spent batteries in a combined solution of Fe^{2+} at 4 g/1000 mL and H_2SO_4 at pH 1.0 was compared with that in H_2SO_4 solution only at same pH. And then 1.0 g of electrode material was placed into 100 mL of both solutions, respectively. The

content of Co and Li in solution as well as the pH and ORP value of solution was monitored periodically during leaching. All the experiments were conducted in triplicates.

2.5. Apparatuses and condition

The pH of the solution was determined using a precise pH meter, ORP was determined by portable ORP meter; the dissolution concentration of Co and Li was determined by atomic absorption spectrophotometer (361MC, Shanghai Precision Scientific Instrument Co., Ltd, China). Morphology change of electrode residues by different bioleaching systems was analyzed by scanning electron microscope (SEM, Hitachi S-4800, Japan) at an accelerating voltage of 20 kV. Micro-area chemical analysis was performed by energy dispersive X-ray analysis (EDX, Oxford) operating at 20.0 keV. Existence behavior of Co^{3+} and Co^{2+} in electrode residues by different bioleaching systems was analyzed by X-ray photoelectron spectroscopy (VG ESCALAB, MK-II, Al $k = 1486.6$ eV, UK).

3. Results

3.1. Contact or non-contact mechanisms identification

The dissolution behavior of the spent batteries trapped or not trapped in three bioleaching systems is shown in Fig. 1. The three bioleaching systems exhibited evident difference in the dissolution behavior and efficiency of both Co and Li. However, in either Co or Li, there was almost no difference in dissolution performance between trapped and not trapped conditions in each bioleaching system. The package of electrode material completely prevented it from contacting directly with leaching bacteria. However, the hindrance to the direct contact did not lead to change in bioleaching behavior and efficiency of both Co and Li in the all three bioleach-

ing systems. The results showed that the dissolution of Co and Li from the spent lithium-ion secondary batteries exclusively depended on the non-contact mechanism, but not on the contact mechanism.

3.2. Dissolution properties of Co and Li and possible indirect mechanism analysis in different bioleaching systems

The time-courses for dissolution dosage of Co and Li, the pH and ORP value in three bioleaching systems are presented in Fig. 2. The dissolution concentration of Co in S + FeS_2 system (1068 mg/L) was higher than that in S system (866 mg/L) or FeS_2 system (989 mg/L) after 5 d of bioleaching; while Li exhibited the highest bioleaching efficiency in S system (441 mg/L) and the lowest in FeS_2 system (353 mg/L). The pH of the S system increased least from 1.0 to 1.54, FeS_2 system increased most to 1.69. The ORP of the FeS_2 system increased first and then decreased, followed by fluctuations on a high-level. These fluctuations resemble the ones displayed on a median level in the S + FeS_2 system. However, the ORP of S system almost had no fluctuations.

The S leaching system with the lowest pH attained the highest extraction of Li, while the FeS_2 leaching system with the highest pH achieved the lowest release of Li. There was a correlation between the release of Li and the pH value of leaching solution. It is suggested that the extraction of Li^+ from the spent lithium-ion secondary batteries was owing to acid dissolution by bio-genetic sulfuric acid in the three bioleaching systems.

Deviant from Li, Co witnessed the lowest bioleaching efficiency in the S leaching system with the highest ability of acid dissolution; while the FeS_2 or S + FeS_2 system with a lower ability of acid dissolution yielded higher leaching efficiency of Co. These findings indicated that the dissolution of Co depended on not only the acid dissolution, but also other mechanisms that may be involved in Co

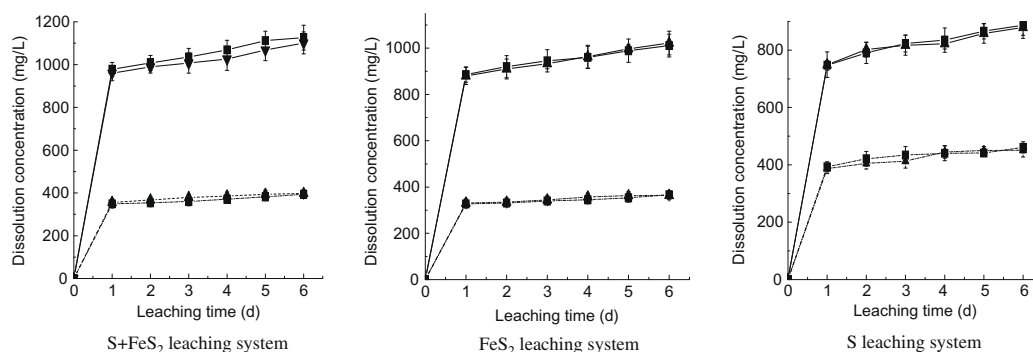


Fig. 1. Comparison of leaching behavior of the encapsulated electrode materials and the not the ones in three bioleaching systems (—■— encapsulated, —▲— not encapsulated; —cobalt ion, --- lithium ion).

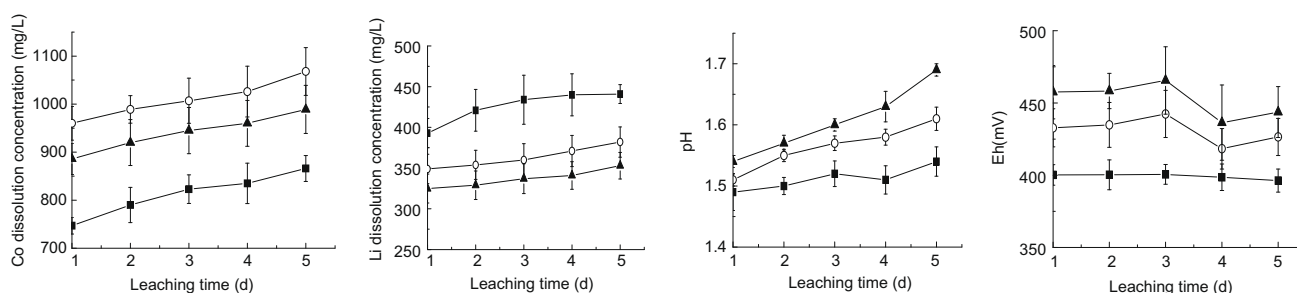
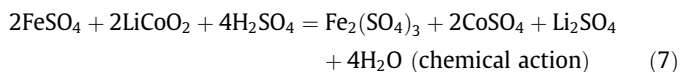
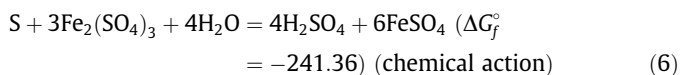
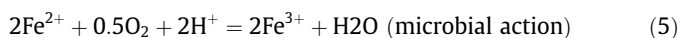
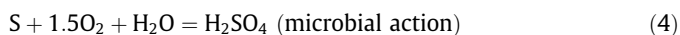
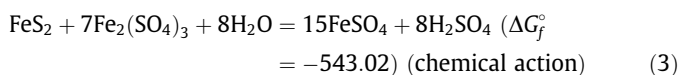
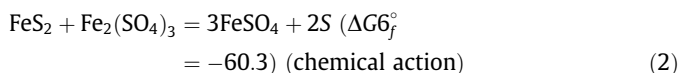
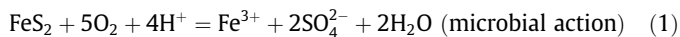


Fig. 2. Time-courses for Co concentration, Li concentration, pH and ORP in bioleaching systems (—■— S leaching system, —▲— FeS_2 leaching system; —○— S + FeS_2 leaching system).

bioleaching by FeS_2 or $\text{S} + \text{FeS}_2$ system. The spent lithium-ion batteries have both soluble Co^{2+} and insoluble Co^{3+} (Yang et al., 2006), although the S leaching system allowed the greatest dissolution of Co^{2+} , the incompetence to Co^{3+} resulted in the lowest bioleaching efficiency.

In the FeS_2 leaching system, metabolism of the energy source generated H_2SO_4 and Fe^{3+} . The H_2SO_4 caused the direct acid dissolution of Co^{2+} ; the Fe^{3+} induced a series of redox reaction as shown by the high-level ORP fluctuation, leading to the formation of the strong reducing agent Fe^{2+} which promoted the reduction dissolution of insoluble Co^{3+} . Specific process was presented as follows (Ou et al., 2007; Wu et al., 2007):



In $\text{S} + \text{FeS}_2$ leaching system, abundant H_2SO_4 was produced by sulfur bio-oxidation (Eq. (4)), therefore acid dissolution of Co^{2+} was stronger than of FeS_2 system. Meanwhile, a lower pH led to greater production of Fe^{3+} from FeS_2 bio-oxidation, as shown in Eq. (1). As a result, more Fe^{2+} was generated via chemical reactions between Fe^{3+} and FeS_2 , resulting in more Co^{3+} reduced and more Co released. Due to a combination of stronger acid dissolution and Fe^{2+} mediated reduction, the $\text{S} + \text{FeS}_2$ system yielded the highest bioleaching efficiency of Co .

3.3. The chemical simulation of acid dissolution by the S bioleaching system

The time-course for the dissolution content of Co and Li in S bioleaching system, chemical acid leaching system and bioleaching-stimulated chemical leaching system is presented in Fig. 3. In the chemical acid leaching system, the maximum dissolution concentrations of 621 mg/L with Co and 303 mg/L with Li were ob-

tained, respectively. In contrast, the bio-genetic acid leaching system witnessed the maximum release concentrations of 920 mg/L for Co and 470 mg/L for Li due to continuous production of sulfuric acid by sulfur bio-oxidation. The bioleaching-stimulated chemical leaching system held almost identical dissolution efficiency on both Co and Li with the bio-acid leaching system by adding external H_2SO_4 . The results further demonstrated that the leaching mechanism of Co and Li in the S bioleaching system was exclusively the bio-acid dissolution.

3.4. Chemical simulation of Co and Li dissolution by the reduction of bio-induced Fe^{2+} in FeS_2 and $\text{S} + \text{FeS}_2$ leaching systems

Comparison of dissolution behavior of batteries between the single H_2SO_4 leaching system and the $\text{H}_2\text{SO}_4 + \text{FeSO}_4$ combined leaching system is presented in Fig. 4. The pH of the $\text{H}_2\text{SO}_4 + \text{Fe}^{2+}$ system rose more rapidly than that of the single H_2SO_4 system, being 2.2 and 2.0, respectively, after 24 h of leaching. Correspondingly, the dissolution content of Li in the single acid system was evidently higher than that in the combined system, further demonstrating that Li release depended on the pH value and was a result of acid dissolution. On the contrary, the dissolution concentration of Co in the combined system was 1.24 times higher than that in the single acid system, displaying a great contribution of Fe^{2+} catalyzed reduction to Co dissolution. Insoluble Co^{3+} was reduced into soluble Co^{2+} by Fe^{2+} , and the resulting Co^{2+} was released into solution by acid dissolution, leading to a rapid increase in ORP due to the generation of Fe^{3+} and a higher pH value due to greater consumption of acid in the combined leaching system. According to these findings, it can be deduced that Fe^{3+} -triggered production of Fe^{2+} in both FeS_2 and $\text{S} + \text{FeS}_2$ bioleaching systems also plays the same important role in the reduction dissolution of Co^{3+} from the spent batteries.

3.5. XPS analysis of the batteries residues from different bioleaching systems

XPS image displayed the existence of Co^{3+} and Co^{2+} in the batteries residues after bioleaching (Fig. 5). Wide peak with the original and FeS_2 samples suggested the coexistence of Co^{3+} and Co^{2+} , while narrow peak with the S and $\text{S} + \text{FeS}_2$ samples suggested the sole existence of insoluble Co^{3+} .

Peaks of Co^{3+} (780.9 eV) and Co^{2+} (780.1 eV) (available in XPS and AES database) were partly overlapped, making it impossible to identify the separated valence states of Co . However, the combined peak width at 780 eV can qualitatively reflect the coexistence of Co^{3+} and Co^{2+} . After bioleaching in S system, all Co^{2+} was released due to the strongest acid dissolution, leaving Co^{3+} alone and its narrower peak. In $\text{S} + \text{FeS}_2$ system, all of Co^{2+} was extracted because of the stronger acid dissolution and some certain Co^{3+} compounds were released due to reduction by Fe^{2+} , leading to

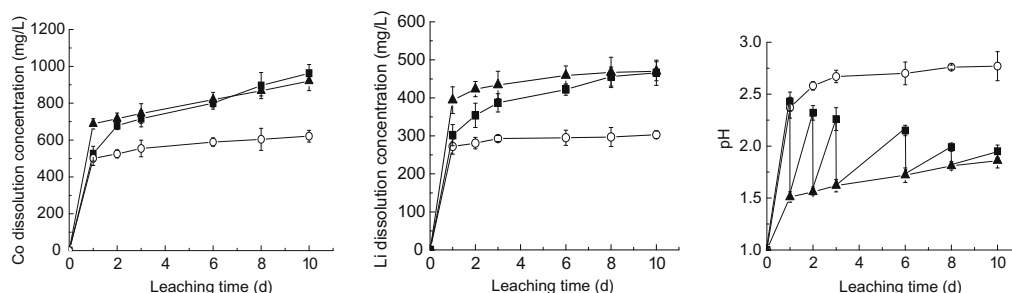


Fig. 3. Comparisons of the bio-acid leaching system, the chemical acid leaching system and the bio-acid-stimulated chemical leaching system in Co dissolution, Li dissolution and pH variation with leaching time, respectively (—▲— bio-acid leaching system; —■— bio-acid-stimulated chemical leaching system; —○— chemical leaching system).

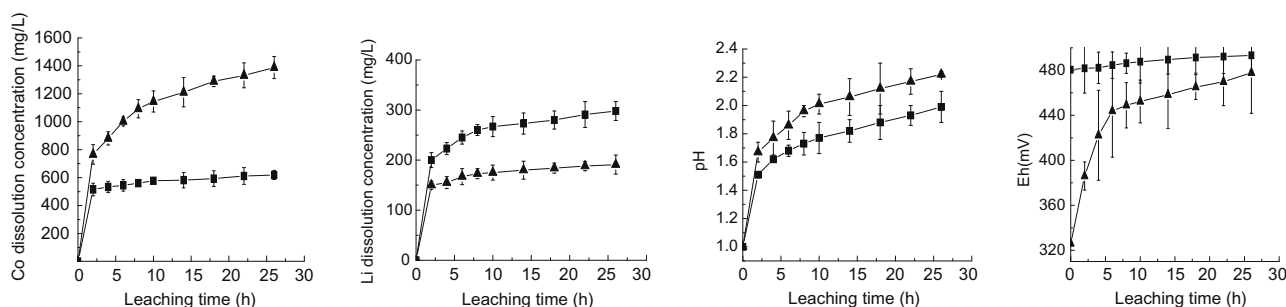


Fig. 4. Time-course for Co release, Li release, pH change and ORP variation in H_2SO_4 leaching system and Fe^{2+} - H_2SO_4 combined leaching system (—■— H_2SO_4 leaching system, —▲— Fe^{2+} - H_2SO_4 combined).

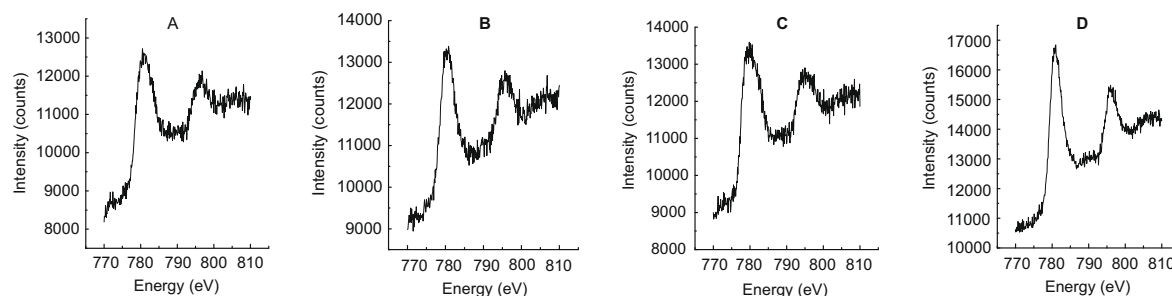


Fig. 5. XPS images of electrode materials residue from different bioleaching systems (A: original sample; B: S leaching system; C: FeS_2 leaching system; D: S + FeS_2 leaching system).

the narrowest peak. Different from S or S + FeS_2 system, although FeS_2 system attains higher bioleaching efficiency of Co than S system owing to Co^{3+} reduction by Fe^{2+} , not all of Co^{2+} was released due to the weak acid dissolution, leaving the coexistence of Co^{3+} and Co^{2+} and the same wide peak as the original sample.

3.6. SEM and EDX analysis of electrode residue in different bioleaching systems

Cobaltic compound LiCoO_2 exists as the frame material in the lithium-ion secondary batteries; however, cobaltous compound CoO evidently appears in the spent ones. In the S leaching system, Co^{2+} in the form of CoO was released by acid dissolution, but Co^{3+} in LiCoO_2 as the frame material was resistant to acid action, accounting for the integrity in the structure of residues (Fig. S1 in Supplementary material). In the FeS_2 leaching system, both Co^{3+} and Co^{2+} were released, respectively, via Fe^{2+} catalyzed reduction and acid dissolution, so the integrity of the particles was destroyed and the border gradually grew blurred, indicating strong leaching ongoing. In the S + FeS_2 leaching system, the particles were fully digested and corrosion pit appeared because of the intense acid dissolution towards Co^{2+} induced by S existence and the intense Fe^{2+} catalyzed reduction towards Co^{3+} under lower pH.

The micro-area chemical analysis of the residual from the FeS_2 bioleaching system by EDX (Fig. S1 in Supplementary material) showed clearly that the remaining electrode materials with integrate structure and distinguishable border contained high-concentration Co, while the micro-area with blurred border witnessed a dramatically reduced concentration of Co, demonstrating that the bioleaching proceeded with structure damage and border melt.

4. Discussion

Although astonishingly diverse groups of bacteria, mould and yeast possess leaching activity, acidophilic sulfur-oxidizing and

iron-oxidizing bacteria are the most widely used microorganisms (Rohwerder et al., 2003). The acidophilic thiobacilli gain energy from the oxidation of elemental sulfur or ferrous ions to meet their growth need, producing sulfuric acid or ferric ions. The bioleaching of metal sulfides depended on both contact and non-contact mechanisms. In most cases, leaching bacteria can attach the mineral sulfide surface and the electrochemical processes take place at the interface between the cell wall and the sulfide surface, resulting in the dissolution of sulfide minerals (Rohwerder et al., 2003). However, the bioleaching of the spent lithium-ion batteries exclusively depended on non-contact mechanism (Fig. 1). Because Fe^{3+} has no direct contribution to the release of Co and Li from the spent batteries, the chemical oxidation by EPS-complexed Fe^{3+} as contact mechanism cannot account for bioleaching. These findings not only confirm that there are evident differences in bioleaching mechanism between the spent secondary batteries and the metal sulfides, but also supply a theoretical basis for the separation of metabolic reactor which generates sulfuric acid or ferric ions and leaching reactor which dissolves metal ions in the designing of practical bioleaching system (Zhao et al., 2008a, 2008b).

In the recent years intensive studies were done on the release of metals from the spent secondary batteries by bioleaching (Cerruti et al., 1998; Zhu et al., 2003; Zhao et al., 2008a, 2008b; Mishra et al., 2008). In bioleaching of the spent Ni–Cd batteries, the indirect mechanisms involved were speculated to be acid dissolution for Cd, both acid dissolution and oxidation extraction by sulfuric acid for Fe, acid dissolution and oxidation extraction as well as reduction liberation by the intermediate reducing compounds from sulfur metabolism for Ni; however, there was no exactly experimental evidence to support the statement (Cerruti et al., 1998). In a comparison studies of bio-dissolution of the spent Ni–Cd batteries using ferrous ions and elemental sulfur as an energy material, respectively, it was proposed that acid dissolution appeared to be the major factor responsible for the release of Ni, Cd and Co; however, there was no detailed and cogent proof to

clearly elucidate the bioleaching mechanism involved (Zhao et al., 2008a).

Lately, the *At. ferrooxidans* was attempted to leaching the spent lithium-ion secondary batteries grown on elemental sulfur and ferrous ion as the energy source, leaching efficiencies of ca. 65% with Co and 10% with Li were attained, respectively; and it was surmised that most of the dissolution of metals (Co and Li) was apparently due to the formation of intermediate reducing compounds by sulfur metabolism (Mishra et al., 2008). Because the bacteria consortium may be involved in cross-feeding to reach optimal conditions for stability (Zhao et al., 2008a), the mixed culture of sulfur-oxidizing and iron-oxidizing bacteria was utilized to leaching the spent lithium-ion batteries in the present studies, and the maximum leaching efficiencies of more than 90% for Co and 80% for Li were obtained, respectively (Fig. 2) by calculating the ratio between the leaching dosage and the total content. The better performance in the present studies maybe owe to the diverse leaching bacteria and energy source substrate which result in the production of diverse metabolic products and consequently introduce diverse leaching mechanisms.

The present study suggested that the bioleaching mechanisms of the spent batteries vary with different metals species and energy source types. With elemental sulfur as an energy source, both Co and Li were extracted from the spent batteries via exclusive acid dissolution by sulfuric acid originated from bio-oxidation of elemental sulfur (Fig. 3), although there were some speculations in the previous reports that the bioleaching of the spent Ni–Cd batteries and lithium-ion batteries maybe in part contributes to the reduction release by the intermediate reducing compounds from sulfur metabolism such as sulfite and thiosulphate (Cerruti et al., 1998; Mishra et al., 2008). Further comparing the Li bioleaching behavior in three bioleaching systems (Fig. 2), it was concluded that acid dissolution is the main bioleaching mechanism for Li extraction independent of the energy matters types. Although the bioleaching mechanism of Li was expounded reasonably, the fact of that nearly 20% of Li remained in the residual reminded us that the mechanism on how this part of Li released was still a question to be solved.

Different from Li, with FeS_2 or $\text{FeS}_2 + \text{S}$ as energy matters, especially the latter, bioleaching of Co was owing to a combined action of acid dissolution and reduction of Fe^{2+} which was produced via a physical–chemical reaction between FeS_2 and Fe^{3+} . The reduction of insoluble Co^{3+} by Fe^{2+} into soluble Co^{2+} and the release of resulting Co^{2+} from the spent batteries by acid dissolution led to higher leaching of Co even at higher pH in FeS_2 or $\text{FeS}_2 + \text{S}$ system than S system (Figs. 2 and 4). In bioleaching of mineral ores, sewage sludge, sediment and fly ash, oxidation attack of Fe^{3+} on the sulfur moiety is a very important mechanism for the release of heavy metals ions from sulfides; in contrast, reduction attack of Fe^{2+} on the Co^{3+} as a very important mechanism accounts for the release of Co from the spent lithium-ion batteries, which has not been reported previously. This is extra difference in concrete bioleaching mechanisms between the spent batteries and metal sulfides. Because the Fe^{2+} worked in coordination with sulfuric acid, the structure of the spent batteries materials was broken down and metal ions were liberated (Fig. S1 in Supplementary material). However, a small amount of Co remained in the residual may be associated with a special structure of certain Co compound resistant to both acid dissolution and Fe^{2+} catalyzed reduction, the release of this part of Co remains to be further studied.

5. Conclusions

The dissolution of Co and Li from the spent lithium-ion battery exclusively depended on the non-contact mechanism, but not on

the contact mechanism. The bioleaching mechanisms of Li in three bioleaching systems were bio-acidic dissolution; Li displayed the maximum extraction efficiency in S system due to the lowest pH. However, the dissolution mechanisms of Co differed with different energy materials. Acid dissolution was the sole mechanism for Co release in the S system, a combined action of acid dissolution and Fe^{2+} mediated reduction accounted for Co release in the $\text{S} + \text{FeS}_2$ or FeS_2 system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2009.06.086.

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